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## **Summary**

Two types of boron nitride nanotubes (BNNTs) were exfoliated into boron nitride nanoribbons (BNNR), which were identified using transmission electron microscopy: (1) commercial BNNTs with thin tube walls and small diameters. Tube unzipping was indicated by a large decrease of the sample's surface area and volume for pores less than 2 nm in diameter. (2) BNNTs with large diameters and thick walls synthesized at NASA Glenn Research Center. Here, tube unravelling was indicated by a large increase in external surface area and pore volume. For both, the exfoliation process was similar to the previous reported method to exfoliate commercial hexagonal boron nitride (hBN): Mixtures of BNNT,  $\text{FeCl}_3$ , and NaF (or KF) were sequentially treated in 250 to 350 °C nitrogen for intercalation, 500 to 750 °C air for exfoliation, and finally HCl for purification. Property changes of the nanosized boron nitride throughout this process were also similar to the previously observed changes of commercial hBN during the exfoliation process: Both crystal structure (x-ray diffraction data) and chemical properties (Fourier-transform infrared spectroscopy data) of the original reactant changed after intercalation and exfoliation, but most (not all) of these changes revert back to those of the reactant once the final, purified products are obtained.

## **Introduction**

In previous research (Ref. 1) commercial hexagonal boron nitride (hBN) was intercalated (i.e., inserted) with ferric chloride ( $\text{FeCl}_3$ ) and then exfoliated (i.e., split into thinner layers). Intercalation with  $\text{FeCl}_3$  is commonly carried out in the carbon industry but has previously been unsuccessful for hBN. It was found that by adding an activation agent—in this case NaF—hBN and  $\text{FeCl}_3$  become reactive. It was subsequently observed that KF or LiF can also be activation agents.

Exfoliated carbon is extensively used in products such as seals, gaskets, foils, heat sinks, and even in water purification applications (Refs. 2 and 3). The newly developed exfoliated hBN could be used in similar but also unique applications for which carbon is not suitable. The unique combination of hBN's high thermal conductivity while simultaneously being an electrical insulator suggests thermal management applications to remove heat generated from high-power devices without disturbing electrical performance. These applications are currently under development (Refs. 4 and 5). Additionally, applications such as seals and gaskets in high-temperature oxidizing or otherwise aggressive environments are of interest because of the superior thermo-oxidative stability of BN relative to carbon.

The research described in this report uses boron nitride nanotubes (BNNTs) instead of commercial hBN for intercalation by  $\text{FeCl}_3$  before exfoliation. Substituting commercial hBN with various types of nanophase BN for the above applications may enable the tailoring of physical or chemical properties to produce final products best suited for the specific applications.

In previous work (Ref. 6), during the process of purification, large BNNTs (more than 100 nm diam.) were found partially exfoliated by  $\text{FeCl}_3$ . It is anticipated that by adding NaF or KF as the activation agent, the exfoliation of BNNTs by  $\text{FeCl}_3$  will be more complete and more pronounced.

Exfoliation of small BNNTs (6 to 70 nm) was reported previously (Ref. 7). Boron nitride nanoribbon (BNNR) was fabricated by exfoliating BNNTs via potassium intercalation. This led to the possibility that  $\text{FeCl}_3$  could also be used for BNNT intercalation and exfoliation to produce BNNR.

## Methods

The previously reported process to obtain pure exfoliated hBN (Ref. 1) was applied to BNNTs. Samples comprising a mixture of BNNTs,  $\text{FeCl}_3$  powder, and an activation agent (NaF or KF powder) were heated in a nitrogen environment at a pressure of 1 atm and a temperature ranging from 250 to 350 °C for 1 day or more, during which intercalation of BNNTs with  $\text{FeCl}_3$  (i.e., insertion of  $\text{FeCl}_3$  into BNNT walls) is anticipated. The products were then exposed to humid air to absorb water—in some but not all runs—and then placed in furnace and heated in air at 500 to 750 °C for 30 min or longer, during which the  $\text{FeCl}_3$  (and water if applicable) in BNNTs would be either evaporated, oxidized to  $\text{Fe}_2\text{O}_3$  directly, or reduced to  $\text{FeCl}_2$  before oxidizing to  $\text{Fe}_2\text{O}_3$ . The chemical reactions and the gas flux ( $\text{FeCl}_3$ ,  $\text{Cl}_2$ ,  $\text{O}_2$ , and water absorbed in the samples) during the reaction would cause exfoliation. The exfoliated BNNTs would then be purified by HCl rinsing.

The degree of BNNT exfoliation was then examined by comparing the reactant BNNTs and the product using transmission electron microscopy (TEM) and surface area and pore volume measurement. Reactions during the process were inferred by comparing the reactant, the intermediate product and the final product using Fourier-transform infrared (FTIR) spectroscopy and x-ray diffraction (XRD) in addition to TEM and surface data.

A Micromeritics Instrument Corp. 3Flex surface characterization instrument was used to measure absorption and desorption of  $\text{N}_2$  at 77 K, from which sample surfaces were characterized via its software. This includes Brunauer-Emmett-Teller (BET) surface area and pore volume measurements for pores smaller than 967.32 Å in radius. Also, the t-plot method was used to obtain data for pores less than 2 nm in diameter (micropores), which was then used qualitatively to demonstrate the differences among the samples.

A Philips CM 200 TEM was used to examine the thin nanosheet products at the level of the individual layers. An Agilent Cary 660 FTIR with an attenuated total reflectance (ATR) accessory was used to characterize infrared bands near the 1300 to 1400  $\text{cm}^{-1}$  and 750 to 800  $\text{cm}^{-1}$  ranges for BN in the products. A Bruker D8 Advance X-Ray Diffractometer was used to find XRD peaks for hBN and identify the impurities in the products.

A Hitachi S-4700II instrument was used to perform field emission scanning electron microscopy (FESEM) to obtain SEM images of the large-diameter BNNTs synthesized in-house at NASA Glenn Research Center (GRC BNNT nanotubes).

Two different types of BNNTs were used in this research: a commercial product, BNNT P1-Beta (Ref. 8) from BNNT, LLC, and a product made at Glenn, GRC BNNT. The former comprises small tubes, most with two- to three-layer walls. The latter comprises large tubes, mostly about 300 nm in diameter with 100-nm-thick tube walls. It was made by exposing a mixture of solid boron and commercially purchased carbon nanotubes (that contains iron catalysts) to 1300 °C pure ammonia.

## Results and Discussion

### Nanoribbon Products Compared to BNNT Precursors (Surface and TEM Data)

Table I is a summary of the surface properties of the products obtained by treating the BNNT P1-Beta with the process of intercalating, exfoliating, and purifying hBN. Note two BNNT precursors were investigated: Reactant A was used as received with KF as the activation agent, and Reactant B underwent heating prior to reaction and used NaF as the activation agent. From this table the following observations were made:

- Micropore surface area and micropore volume of BNNT P1-Beta (Reactants A and B) were greatly reduced for Products A and B, respectively, after the intercalation-exfoliation-purification reactions. Since micropores are pores with small diameter ( $\leq 2$  nm), micropore area and volume include areas and volume inside the small BNNT tube walls. Therefore, a large decrease of micropore surface and

volume indicates a decrease in the number of small tubes. This is consistent with the previously reported “unzipping” of BNNTs resulting from exfoliation (Ref. 7).

- BET surface area and pore volume of as-received BNNT P1-Beta (Reactant A) increased noticeably to the values for Product A after the intercalation-exfoliation-purification reaction where KF was the activation agent. The increase of BET surface area suggests that in addition to the tube unzipping described above, the as-received BNNT P1-Beta could also be exfoliated to some degree. The large increase of pore volume (radius  $\leq 967.32$  Å) may be explained as caused by an increase of pores in the aggregate of walls of the exfoliated small tubes.
- After preheating as-received BNNT P1-Beta in 450 °C air, its reactivity changes. Treating this preheated BNNT material (Reactant B) with the intercalation-exfoliation-purification process using NaF as the activation agent did not result in BET surface area or pore volume increases. It appears that the intercalation-exfoliation-purification process did not cause the intended reactions of intercalation and/or exfoliation. The possible explanation for the apparent loss of the reactivity includes: air preheating could damage BNNTs, or the activation agent NaF could be less reactive in this case.

Table II is a summary of the surface properties of the products obtained by treating the GRC BNNT nanotubes (Reactant C, synthesized in-house at the NASA Glenn Research Center, most with a ~300-nm diam. and 100-nm-thick tube wall) with the process of intercalation, exfoliation, and purification. From this table the following observations were made:

- Products C1, C2, and C3 have BET surface areas and pore volume (radius  $\leq 967.32$  Å) much larger than their Reactant C. This is likely the result of exfoliation where tube walls of these large BNNTs exfoliate.
- BET surface area and pore volume of these BNNTs increased during the first intercalation-exfoliation-purification cycle (Product C1). Subsequent cycles of repeated intercalation-exfoliation did not result in further increases of BET surface areas and pore volumes. It in fact had an apparent reverse effect of decreasing BET surface areas and pore volume (Product C2). The reason is not known. However, it could be explained as the result of a previously discussed phenomenon: When the exfoliated pieces became sufficiently small, they could behave like small hBN sheets that stack up and fused into large units over time.
- Reactant C contains no micropores (diameters less than 2 nm). When exfoliation was enhanced by water boiling from inside the tube walls at a high heating rate, Products C1 and C2 contain no micropores either. When exfoliation was conducted at slow heating without the presence of water, Product C3 contains noticeable amount of micropores. It appears that fast and forceful mass transfer from regions in the tube wall to its surroundings either creates pores of larger sizes or causes complete wall separation (i.e., exfoliation), but generates no micropores.

TEM and FESEM were used to directly observe the reactants and products of the intercalation-exfoliation-purification process. The morphology data thus obtained is then compared to the surface data interpretation in the above section.

TEM images of the as-received small BNNT P1-Beta (Reactant A in Table I) are presented in Figure 1. Individual tubes can clearly be observed. Many of them are covered by materials that have been described as carbonaceous absorbates (Ref. 7). This is consistent with the observation that the grey as-received sample became whiter after 450 to 750 °C heating in air, when black-colored carbon would be removed by oxidation. The images are similar to those obtained by the manufacturer (Ref. 8). After treating this as-received BNNT with the intercalation-exfoliation-purification process using KF as the activation agent, TEM was again used to examine the product (Product A in Table I). The images thus obtained are presented in Figure 2. Tube unzipping (Fig. 2(a)) and tube wall exfoliation (Figs. 2(b) and (c)) can easily be identified. These are believed to be the cause of the decreased micropore area and increased BET surface area, as seen in Table I. In addition, the unzipped tubes and the exfoliated tube

walls appear to roll together into aggregates of nanoribbons (Fig. 2(d)). The aggregates are believed to be porous, which contributes to the sample's large pore volumes described in Table I.

An FESEM image of the GRC BNNT nanotubes (Reactant C in Table II) is presented in Figure 3. The sizes of the tubes are similar to those of the carbon nanotubes that were used for BNNT synthesis. After treating this as-received BNNT with the intercalation-water absorption-exfoliation-purification process using NaF as the activation agent, both FESEM and TEM were used to examine the product (Product C1 in Table II). FESEM shows general morphological features of the products. Figure 4(a) shows the product includes two parts: (1) cotton-like regions, where the structures are beyond the resolution of FESEM and (2) regions of tubes similar to the BNNT precursor (Fig. 3). A close look into the tube regions reveals that the tubes are actually aggregates of exfoliated sheets, the structures of which are again beyond the resolution of FESEM. For TEM, numerous images taken from different parts of the samples gave similar images, as shown in Figures 4(d) and (e). It appears that Reactant C's tube walls on the order of 100 nm thick were completely exfoliated into nanoribbons about 5 nm thick, and the nanoribbons rolled together into an aggregate of varying degrees of compactness. The exfoliation would cause a large increase of BET surface area. The formation of aggregates would create regions between the nanoribbons as pore volume. Both of them were consistent with the surface changes from Reactant C to Product C1 as described in Table II.

The observed phenomenon that nanoribbons from BNNT exfoliation rolled together into aggregates is different from the previously observed phenomenon that nanosheets from hBN exfoliation tend to stack together and eventually fused into larger crystals. It is believed that fusing nanomaterials into hBN (i.e., matching a large number of boron atoms in one piece of the nanomaterial to a large number of nitrogen atoms in another piece, and vice versa) is possible if the pieces of nanomaterial are flat two-dimensional nanosheets, but is difficult if they are one-dimensional nanoribbons with curves.

### Reactions Inferred From XRD and FTIR Data

The process used in this research was previously developed to intercalate-exfoliate-purify hBN. The above TEM and surface data on the original reactant and the final products suggest such reactions indeed happened with BNNTs as well. To further investigate this, examinations were made to see how data obtained from XRD and FTIR would change as the BNNTs were treated from being the reactant to the intermediate and finally the products. The observed BNNT changes during the process was then compared to those of hBN.

Figures 5(a) and (b) are XRD patterns of the small BNNT P1-Beta (Ref. 8) BNNTs and the GRC BNNT nanotubes, respectively, taken throughout the intercalation-exfoliation-purification process. In both cases, all of the reactants' BNNT peaks disappeared after the step of intercalation, and did not appear again until the end of final purification. Since thin BNNT walls (e.g., two to three layers (Ref. 8)) do not have XRD peaks, the disappearance of XRD peaks do not give information about how thin walls change. It does, however, suggest that thick tube walls in the sample become disordered, likely due to the presence of the intercalated chemicals in the layers. This phenomenon is similar to that with hBN, except hBN has larger and sharper BN peaks. During the period between the end of intercalation and the end of purification, hBN's large peaks decrease in height, but do not completely disappear (Ref. 1).

Figures 5(a) and (b) also show the presence of KCl in the sample. It appears that KF reacted with  $\text{FeCl}_3$  to produce KCl and some fluorine compounds that activate intercalation, much in the same way that NaF reacts with  $\text{FeCl}_3$  to produce NaCl and some fluorine compounds that activate intercalation (Ref. 1).

Figures 6(a) and (b) are FTIR spectra of the small BNNT P1-Beta and the GRC BNNT nanotubes, respectively, taken throughout the intercalation-exfoliation-purification process. In both cases, positions, sizes, and shapes for the two BNNT peaks at  $1300$  to  $1400\text{ cm}^{-1}$  and  $750$  to  $850\text{ cm}^{-1}$  changed when the reactant becomes the intermediate products after the first step (i.e., intercalation), and continued to be very different from the original state, but for the most part reverted back to the original state at the end of the final purification. This phenomenon again is similar to hBN in its trend, except the changes are smaller for the BNNTs than for hBN (Ref. 1).



## Potential Applications

BNNR has been studied for both fundamental interests as well as engineering applications, as it is theorized to possess a wide range of electronic, optical, and magnetic properties arising from various edge structures and terminations (Ref. 7). In addition, for the development of hBN as a high-thermal-conductivity electrical insulator for thermal management (Refs. 4 and 5), substituting commercial hBN for BNNTs described in this report or other types of nanophase hBN described elsewhere (Ref. 1) may allow for the tailoring of physical or chemical properties of the final products best for the specific application. Synthesis and characterization of composites made from BNNT and BNNR are currently under investigation.

## Conclusions

The previously developed method to intercalate, exfoliate, and purify hexagonal boron nitride (hBN) was successfully applied to boron nitride nanotubes (BNNTs). Briefly, BNNTs were treated sequentially by the following steps: intercalation with  $\text{FeCl}_3$  using NaF or KF as an activation agent; (in some but not all experiments) hydrated in room-temperature humid air; exfoliated in 500 to 750 °C air; and purified in HCl. Analysis of x-ray diffraction and Fourier-transform infrared data on the reactants and then intermediate and final products led to the inference that chemical reactions for the BNNTs during this process are the same as those for hBN. Transmission electron microscopy and surface data indicate the final products were unzipped BNNTs and/or boron nitride nanoribbons (BNNRs). If the BNNRs were made from the BNNT, LLC, P1-Beta BNNTs, the exfoliated and purified products had Brunauer-Emmett-Teller (BET) surface areas in the 200 to 250  $\text{m}^2/\text{g}$  range and pore volumes in the 0.8 to 1.1  $\text{cm}^3/\text{g}$  range. If the original reactant was the GRC BNNT nanotubes made from ammonia, solid boron, and carbon nanotubes, the BET surface areas were 150 to 200  $\text{m}^2/\text{g}$  and pore volumes were 0.5 to 0.7  $\text{cm}^3/\text{g}$ .

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TABLE I.—SURFACE PROPERTIES OF PRODUCTS OBTAINED BY TREATING  
BNNT P1-BETA<sup>a</sup> BORON NITRIDE NANOTUBES (BNNT) WITH  
INTERCALATION, EXFOLIATION, AND PURIFICATION

Property	Reactant A	Product A	Reactant B	Product B
Brunauer-Emmett-Teller (BET) surface area, m <sup>2</sup> /g	208	259	262	213
Micropore area, m <sup>2</sup> /g	30	7	51	14
Micropore volume, cm <sup>3</sup> /g	0.014	0.0017	0.024	0.0060
Pore volume, cm <sup>3</sup> /g (radius ≤967.32 Å)	0.65	1.13	0.79	0.81
Note on intercalation-exfoliation-purification process	As-received BNNT (Reactant A) was treated without preheat and KF as activation agent.		Reactant B obtained by preheating as-received BNNT in 450 °C air and NaF as activation agent.	

<sup>a</sup>Reactants A and B are from two separate purchases of BNNT P1-Beta BNNTs (BNNT, LLC) (Ref. 8).

TABLE II.—SURFACE PROPERTIES OF PRODUCTS OBTAINED BY TREATING GRC BNNT<sup>a</sup>  
BORON NITRIDE NANOTUBES WITH INTERCALATION, EXFOLIATION, AND PURIFICATION

Property	Reactant C	Product C1	Product C2	Product C3
Brunauer-Emmett-Teller (BET) surface area, m <sup>2</sup> /g	52	204	156	192
Micropore area m <sup>2</sup> /g	(b)	(b)	(b)	5.5
Micropore volume cm <sup>3</sup> /g	(b)	(b)	(b)	0.0013
Pore volume cm <sup>3</sup> /g (radius ≤967.32 Å)	0.21	0.71	0.49	0.50
Note on intercalation-exfoliation-purification process	(c)	(d) NaF activation agent	Same as C1, repeated three times	(d) KF activation agent

<sup>a</sup>Most having ~300-nm diameters and 100-nm-thick tube walls.

<sup>b</sup>The values were so small that computer software gave negative numbers.

<sup>c</sup>Reactant C was BNNT synthesized by exposing a mixture of boron powder and carbon nanotubes to 1300 °C ammonia for 1 h. The as-synthesized BNNT (Reactant C) was purified by preheating with 35-wt% HCl and 750 °C air before the process of intercalation-exfoliation-purification.

<sup>d</sup>For C1, the intermediate product after intercalation was allowed to absorb water before exfoliation at high heating rate. For C3, the intermediate product without water was exfoliated at slow heating rate.

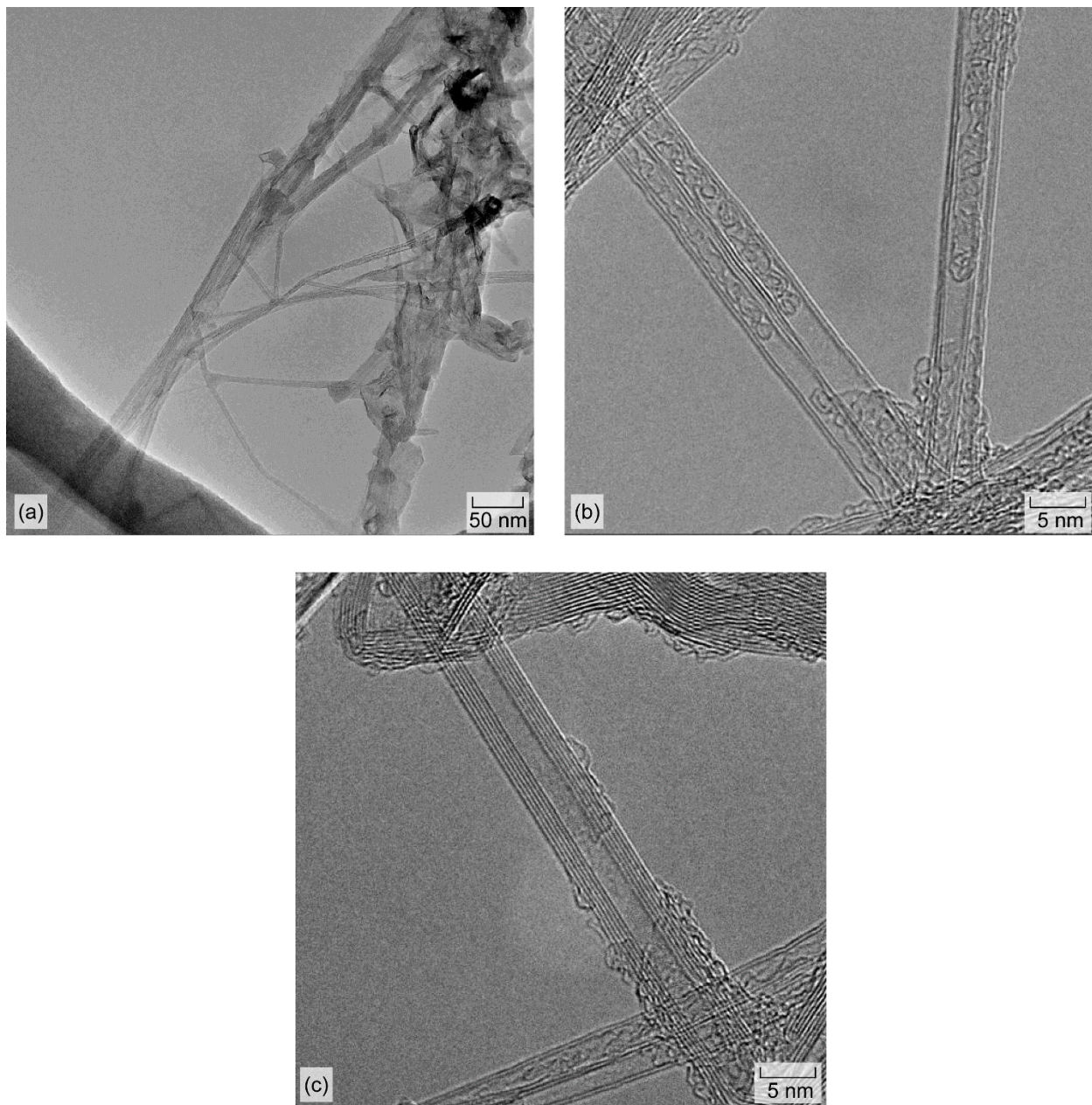


Figure 1.—Transmission electron microscopy (TEM) micrographs of BNNT P1-Beta boron nitride nanotubes (BNNTs) obtained from BNNT, LLC (Reactant A in Table I). (a) Sample includes individual tubes as well as tube aggregates. (b) Tubes with two walls. (c) Multiwalled BNNTs.

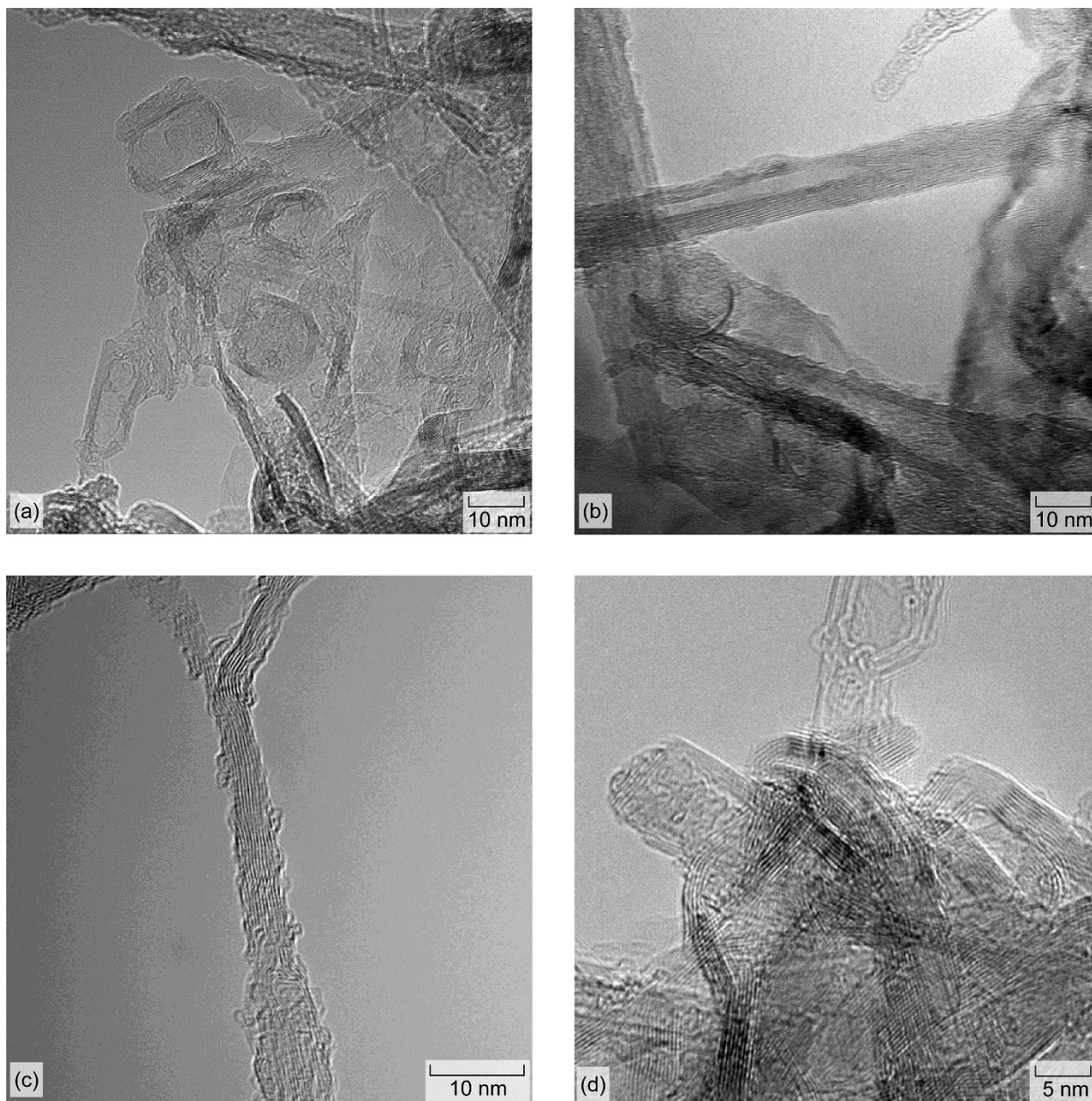


Figure 2.—Transmission electron microscopy (TEM) micrographs of BNNT P1-Beta boron nitride nanotubes after being treated with intercalation-exfoliation-purification process (Product A in Table I). (a) Tube unzipped, exfoliated, and broken into short sections. (b) Long tubes unzipped and exfoliated. (c) Individual exfoliated multiwalled tubes. (d) Aggregate of exfoliated boron nitride nanoribbons.



Figure 3.—Field emission scanning electron microscopy (FESEM) micrographs of GRC BNNT boron nitride nanotubes (Reactant C in Table II) prepared by exposing mixture of boron powder and carbon nanotubes to 1300 °C ammonia.



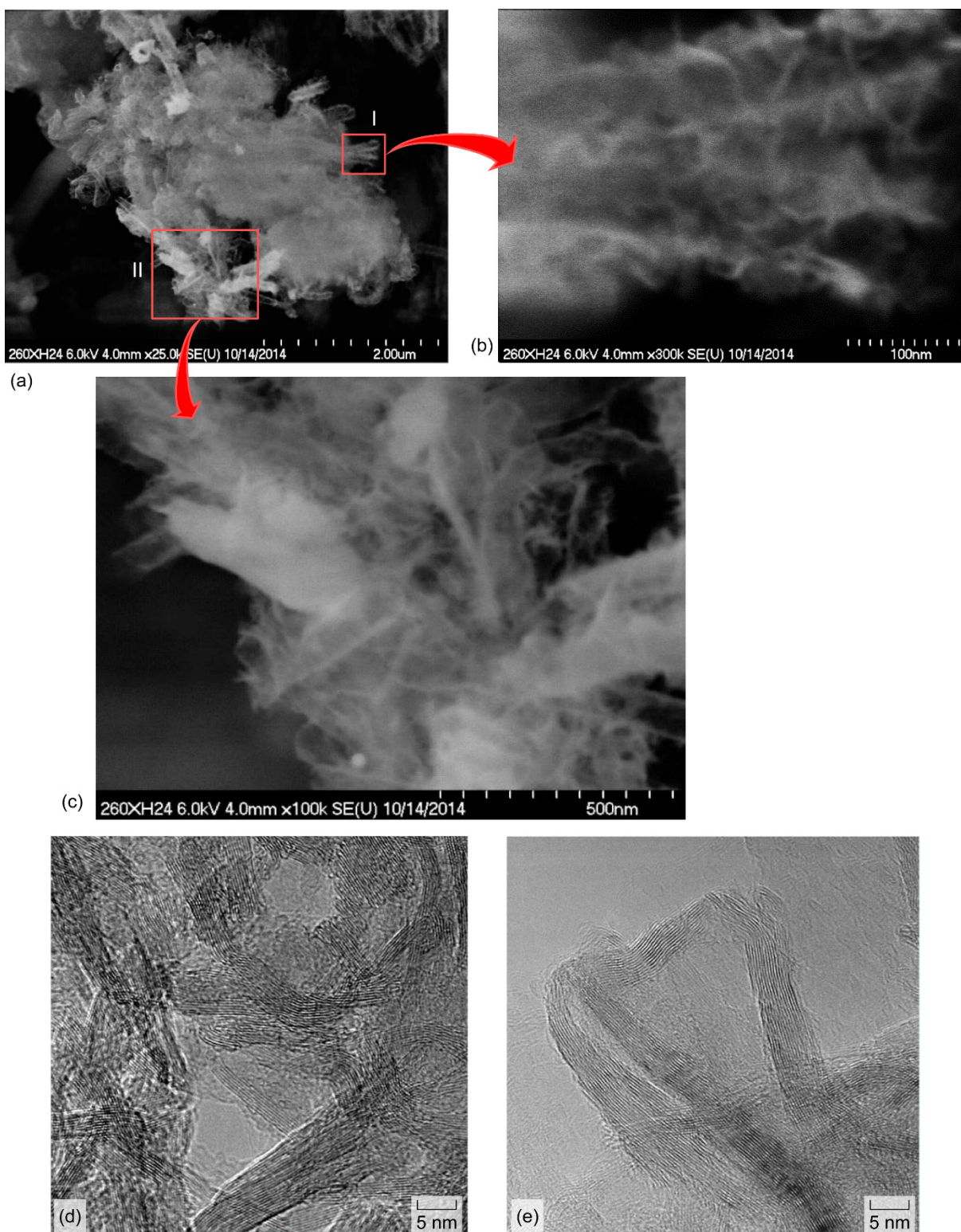


Figure 4.—Micrographs of GRC BNNT boron nitride nanotubes after exfoliation (Product C1 in Table II). (a) Field emission scanning electron microscopy (FESEM) image, showing cotton-like regions and tube regions. (b) FESEM of fine structure in region I of part (a). (c) FESEM of fine structure in region II of part (a). (d) Compact transmission electron microscopy (TEM) sample of boron nitride nanoribbon aggregate in region beyond FESEM resolution. (e) Less compact TEM sample of boron nitride nanoribbon aggregate in region beyond FESEM resolution.

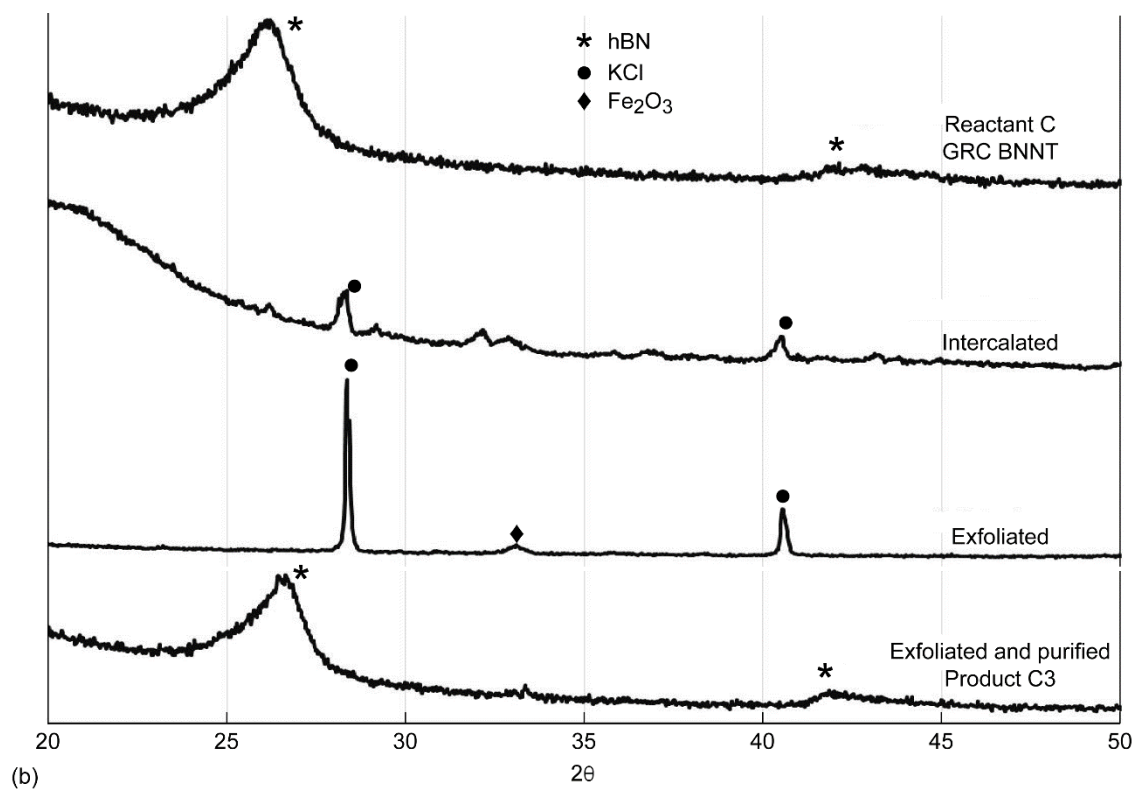
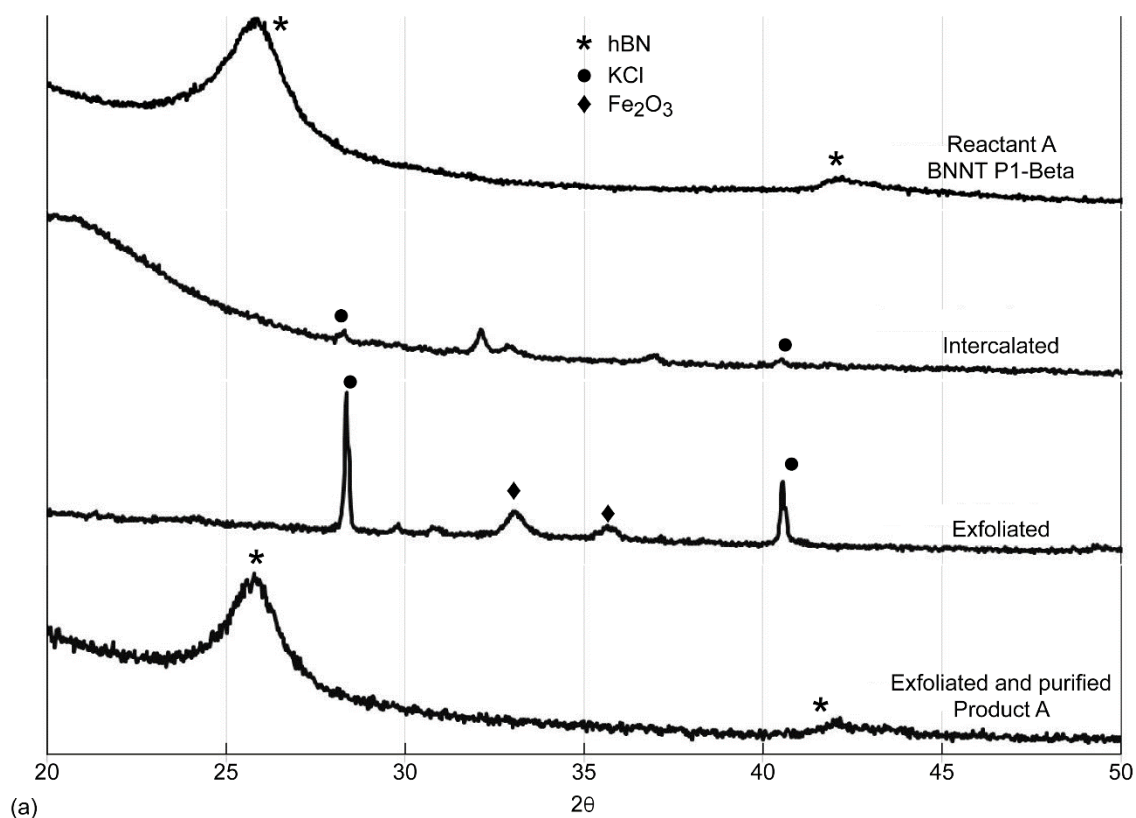


Figure 5.—X-ray diffraction (XRD) patterns of boron nitride nanotubes throughout intercalation, exfoliation, and purification process. (a) BNNT P1-Beta (BNNT, LLC) sample. From Reactant A to Product A in Table I. (b) GRC BNNT boron nitride nanotube sample. From Reactant C to Product C3 in Table II.

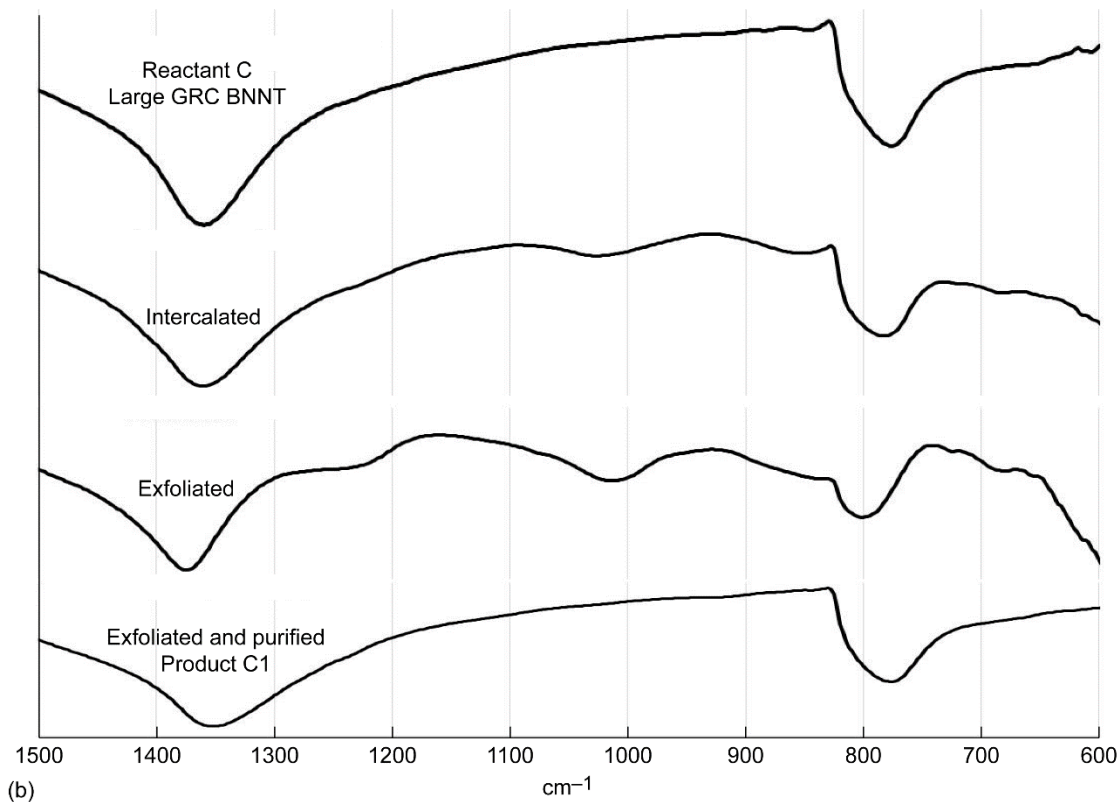
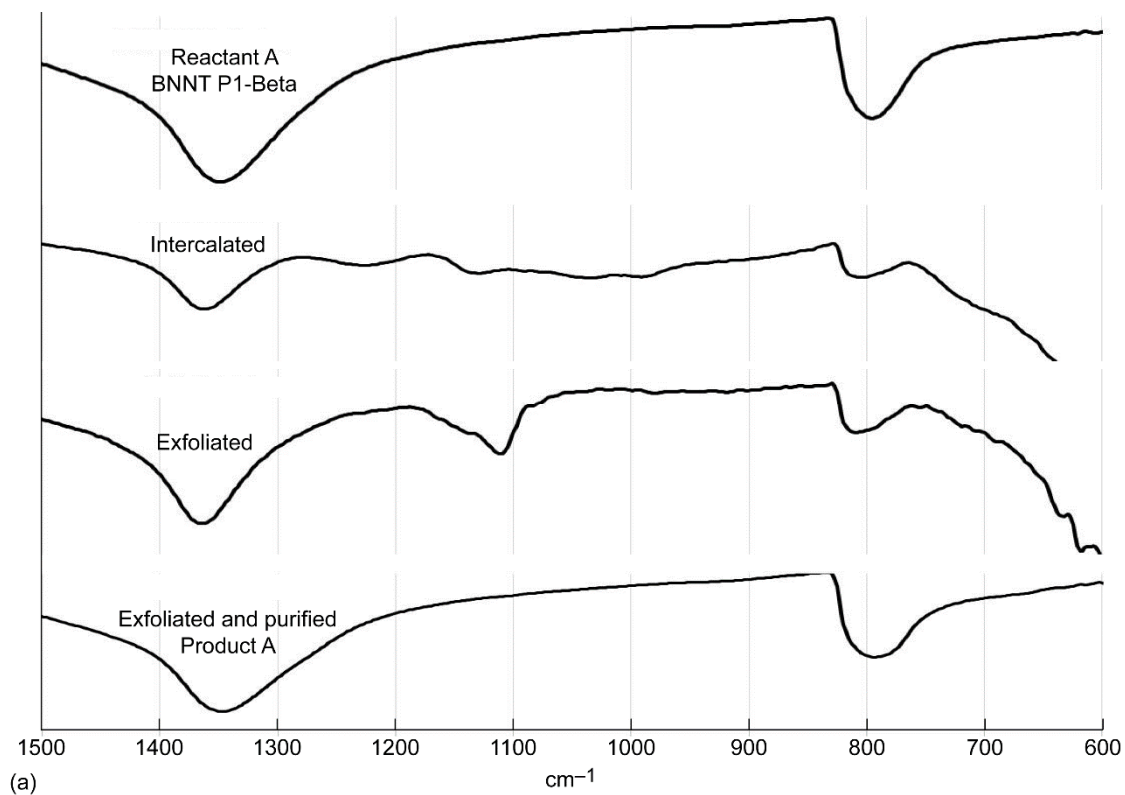


Figure 6.—Fourier-transform infrared (FTIR) spectra of boron nitride nanotubes (BNNTs) throughout intercalation, exfoliation, and purification process. (a) BNNT P1-Beta (BNNT, LLC) sample. From Reactant A to Product A in Table I. (b) GRC BNNT boron nitride nanotube sample. From Reactant C to Product C1 in Table II.





